

Structural and Spectral Aspects of Cerium doped ZnO Nanocrystals

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ABSTRACT

Pristine and Ce doped ZnO nanopowders were synthesized by low temperature precipitation technique. The phase purity was confirmed by XRD. A particle size of 20nm is obtained via TEM studies. Spherical morphology is obtained for 0.2mol% doped ZnO powders which are due to crucial role played by the non-ionic surfactant ethylene glycol during the synthesis. The emission for pristine ZnO is obtained at 383nm and is assigned to a contribution due to free exciton recombination through exciton-exciton collision processes. For Ce doped sample, double peak emission at 493nm and 530nm is observed for green band and could be contribution of different influential factors of Ce ions. Therefore the shift towards visible range of the emission spectra shows its potential use in luminescent flat displays and other optical and other photonic applicability.

Key words: ZnO; Nanocrystalline material; Exciton; Energy transfer; Luminescence.

INTRODUCTION

ZnO holds promises as a material for blue/UV emission, alternative to GaN, which could be a cheap, transparent conducting oxide material, for electronic circuits which are transparent in the visible or for the semiconductor spintronics¹. ZnO has unique ability to attain different morphological forms when different

processing parameters are varied during synthesis. Its band gap is 3.37eV and possesses very high binding energy (~60 MeV). The wealth of different morphological forms of ZnO powders (cones and spherulites) was reported earlier², for extending the domain of our study, herein, we have tried to explore the spectroscopic characteristics of Cerium doped ZnO. The rare earth (RE) ions doped

materials have gained fresh momentum in luminescence research due to their characteristic emission possibilities with higher reproducibility. Ce is the first member of lanthanide series and can possess anomalous emission characteristics (emission can extend its domain from UV to red region of electromagnetic spectrum). Earlier we have already reported such anomalous behavior of Ce^{3+} in $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ ³. The present work is carried out to fulfill two objectives: a.) Controlled single step synthesis of spherical ZnO nanocrystals using solution route and, b.) Influence of Ce^{3+} doping in the present host.

EXPERIMENTAL

Synthesis

GR grade (purity > 99%) Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), urea ($(\text{NH}_2)_2\text{CO}$), and ethylene glycol (EG) ($\text{C}_2\text{H}_6\text{O}_2$), were used as precursors for synthesis reaction. 0.5g of zinc acetate is dissolved in 50 ml EG, (used as capping agent and solvent). 1.5g of urea was added into this solution and the temperature was raised to 150°C (time ~ 2 hrs). A white precipitate of undoped ZnO was obtained. The precipitates were separated by centrifugation and washed several times with quadruple distilled water and methanol to remove the excess EG and/or traces of impurities. Thereafter, the samples were dried in ambient conditions and kept for further characterization. Same procedure was adopted for the synthesis of ZnO: Ce (0.2mol %) nanocrystals, except, appropriate amount of cerium nitrate was dissolved and added to the solution of zinc acetate and ethylene glycol at the beginning of the reaction process.

Characterization

X-ray diffraction patterns were obtained on Rigaku MiniFlex II instrument with Cu-K α radiations ($\lambda = 1.54060\text{\AA}$) at room temperature operated at 30 kV and a scan speed of $2^\circ/\text{min}$. The morphology was obtained on JEOL JSM 6390 scanning electron microscope (SEM). TEM measurements were carried out on Philips CM200 instrument having the operating voltage of 200kV and a resolution of $2.4\text{\AA}$. The photoluminescence spectrum was obtained with Hitachi F-4500 spectrophotometer with the scan speed $240\text{nm}/\text{min}$.

RESULTS AND DISCUSSIONS

XRD Results

The X-Ray diffraction pattern for crystalline nature pristine and doped ZnO nano-powders is shown in *Figure 1*. Comparing the XRD pattern, with Joint committee powder diffraction standards (JCPDS file no 80-0075), no additional signatures, of any other intermediate phase could be seen. In the XRD patterns, the peak broadening features has been assigned to the smaller crystallite size of as-synthesized powders. The apparent crystallite size is calculated using Scherrer equation and is approximated at 26 nm. The equation is

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

Where k is close to unity, θ is Bragg angle of $\{h\ k\ l\}$ reflections, and D is the crystallite size and λ is wavelength of X-rays,

SEM and TEM studies

The SEM pattern for Ce (0.2 mol %) doped ZnO nanocrystals is shown in *Figure 2*. The crystallites have spherical morphology. There are numerous factors that can affect the shape and size of the crystallites during synthesis procedure. In the present case, we anticipate that the spherical morphology is due to the crucial role played by the ethylene glycol during synthesis of ZnO nanocrystals. Ethylene glycol (EG) is mainly absorbed at the surface of the metal oxides which is an important non-ionic surfactant with uniform and ordered chain like structure. The organic ligands formed by EG have high binding affinities. It promotes for the self assembly by interacting between them on the surface itself which avoids the interaction of the particles themselves. In addition, the ligands involve self assembly is likely to generate single crystalline architecture that usually couldn't be obtained from the conventional processes. Hence, we anticipate that during the self assembly, at low concentrations, ZnO particles rotated themselves and aggregated through ethylene glycol while sharing same crystallographic planes leading to spherical morphology.

To confirm the size of the ZnO nanocrystals TEM studies are carried out. The TEM pattern is shown in *Figure 3*. As noticed, an average particle size of 20nm is approximated in the present case. A good correlation is found to exist between mathematical calculations from Scherrer formula (XRD studies) and those obtained via TEM studies.

PHOTOLUMINESCENCE (PL)

Pristine ZnO

Two characteristic bands are observed in the spectrum of

photoluminescence of ZnO powders *Figure 4*. The emission spectra of ZnO sample show a near-band-edge UV line ($\lambda=383\text{nm}$) followed by a deep level luminescence in lower energy regime ($\lambda=485\text{nm}$ and $\lambda=510\text{nm}$, $\Delta\lambda=25\text{nm}$). Lower energy bands originate from the various defects depending upon the growth technique and can decrease the emission efficiency of the UV emission while increasing the lasing action threshold. Luminescence features also depend on other crucial factors which includes solvent, atmosphere, starting materials, etc and is attributed to different processing conditions (quenching centers) during synthesis process.

In the present case, the higher energy UV-band is assigned to the free exciton recombination through exciton-exciton collision processes. On the other hand, the lower energy green emission band can be assigned to the presence of oxygen vacancies or to some type of defects formed during synthesis of ZnO nanopowders. The probable defects can be interstitial Zn or O (Zn_i or O_i), zinc vacancy (V_{Zn}) or the oxygen antisite (O_{Zn}). The exact nature of defects can only be determined after further experimentation like calcining effects (on PL) of ZnO in oxygen or ammonia atmosphere or through ESR mapping etc.

Ce doped ZnO:

The normalized PL spectrum for Ce doped (0.2 mol %) ZnO nanocrystals are shown in *Figure 5*. The emission possesses three well defined bands situated at lower wavelength 408nm band and higher wavelength 493nm and 530nm for 330nm excitation wavelength. For the UV-band, slight red shift is observed for doped ZnO. It is anticipated that as the dopant is incorporated into the host matrix, strain

increases. Consequentially, some new types of defects are expected to be formed. The introduced dopant ions might shape a shallow energy level near valence band. Hence, we assign the red shift to the defects and the probable shallower energy levels⁴. For Ce doped sample, with the same excitation of 330nm, the higher wavelength green band has two well defined maximums. Ce can attain two states when incorporated into any matrix, i.e. Ce^{3+} and Ce^{4+} f-d transitions are susceptible to field effects and hence, 5d state of Ce^{3+} splits into two states namely E_g and T_{2g} with broad FWHM characteristics. Here, we anticipate that, the higher wavelength PL emission (green band) can be due to three reasons: a.) the emission is obtained from the transitions between higher E_g level to lower lying $^2F_{5/2}$ and $^2F_{7/2}$ f-states or, b.) the formation of some new type of defects and c.) due to some type of energy transfer from host to Ce^{3+} sites leading to Ce^{3+} emission characteristics (as the excitation wavelength is same for pristine and doped samples). To determine the main centers causing the increased green emission, we carried out mathematical treatment for the complicated profile of luminescence spectrum. Gaussian deconvolution function was applied to estimate the peak positions and spectral width of present spectra. As defined by Dorenbos^{5,6}, the separation between two bands should be around 2000cm^{-1} for Ce^{3+} emission possibilities as in CaO it is about 1800cm^{-1} . In the present case, the separation is 1416cm^{-1} only. Hence, looking at the results, we realize the need for further studies like lifetime measurements, etc. is going on. At this stage when the excitation wavelength is common for pristine and doped samples, the possibility of energy transfer from host to

Ce^{3+} cannot be neglected. The studies in this direction are in progress.

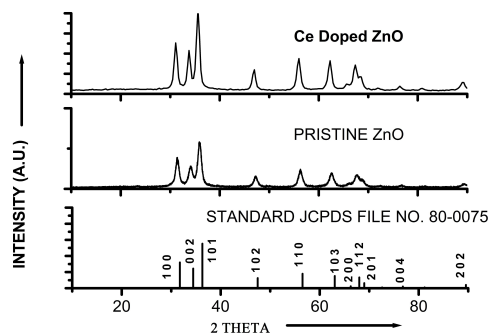


Figure1. X-ray diffraction pattern for pristine and Ce (0.2mol%) doped ZnO nanopowders.

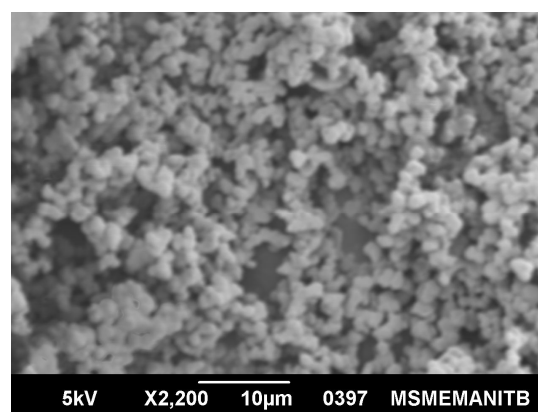


Figure2. SEM micrograph for Ce (0.2mol%) doped ZnO

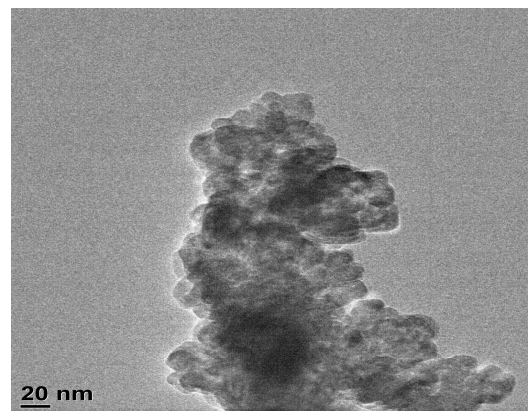


Figure3. TEM results for (0.2mol%) doped ZnO

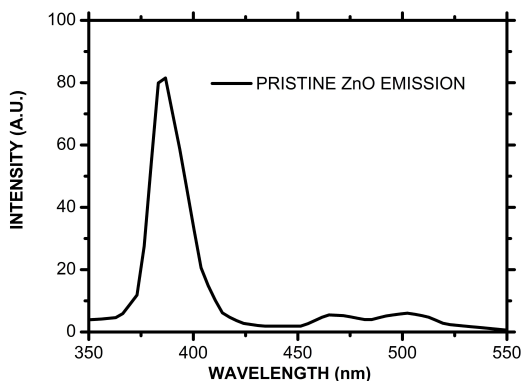


Figure 4. PL spectra for pristine ZnO

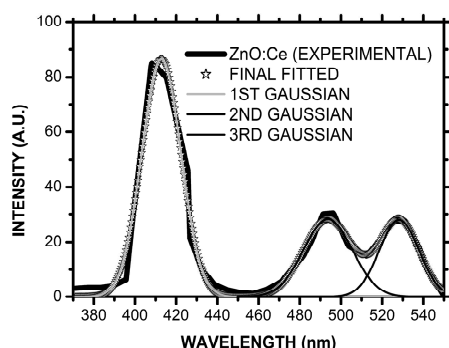


Figure 5. PL spectra for Ce (0.2mol%) doped ZnO

CONCLUSION

ZnO nanocrystals with spherical morphology have been synthesized by cost effective precipitation technique for industrial applications. Spherical morphology is designated to the crucial role played by the ethylene glycol during synthesis. TEM results indicate that the crystallite size in the as prepared nanocrystals is 20nm. For pristine samples, PL is observed at 383nm (near-UV region). For Ce doped sample, three well defined emission bands are obtained at 408nm, 493nm and 530nm. The higher wavelength bands are assigned to either emission from

Ce lowest E_g band (5d state) due to the possibilities of energy transfer from host to Ce^{3+} sites or due to defects. The facile, reproducible, and effective route presented here provides a useful method for the RE^{3+} doped ZnO system. The high crystal quality of the Ce doped nanocrystals and good optical properties under room temperature make it a candidate of optical materials for the applications in the future.

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